

# Nanopercolation

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We investigate through direct molecular mechanics calculations the geometrical properties of hydrocarbon mantles subjected to percolation disorder. We show that the structures of mantles generated at the critical percolation point have a fractal dimension  $d_f \approx 2.5$ . In addition, the solvent access surface  $A_s$  and volume  $V_s$  of these molecules follow power-law behavior,  $A_s \sim L^{\alpha_A}$  and  $V_s \sim L^{\alpha_V}$ , where  $L$  is the system size, and with both critical exponents  $\alpha_A$  and  $\alpha_V$  being significantly dependent on the radius of the accessing probing molecule,  $r_p$ . Our results from extensive simulations with two distinct microscopic topologies (i.e., square and honeycomb) indicate the consistency of the statistical analysis and confirm the self-similar characteristic of the percolating hydrocarbons. Due to their highly branched topology, some of the potential applications for this new class of disordered molecules include drug delivery, catalysis, and supramolecular structures.

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In recent years there has been a great scientific and technological advance in the design and development of new materials. The use of molecular modelling techniques is certainly responsible for the significant contribution to this activities of most theoretical and computational studies [1]. New improved catalysts, original reactive processing and the chemistry and physics of polymers are just a few among several examples representing the multitude of research fields that have been successfully approached employing molecular modelling tools. For instance, an important research work with potential applications in the field of polymer science refers to the real possibility of manipulating and controlling the properties of complex macromolecules through adequate polymerization routes and specific chemical processing strategies.

An inspiring example where molecular modelling plays an important role in polymer science is the design and characterization of *functional* polymers. By definition, the term functional refers to the property of some molecules that contain reactive end-groups to preserve the integrity of their molecular backbone while participating in chemical reactions. Because *dendrimers* are highly branched macromolecules and, therefore, have a large number of end-groups, they represent a natural class of candidates for substrates of functional polymers. Among many possible applications for dendrimers, we mention their potential use for drug delivery [2], and the ability to act as catalysts supports [3] and supramolecular structures [4]. In a recent theoretical study, the molecular topology and surface accessibility of dendrimers have been investigated through extensive molecular mechanics and molecular dynamics simulations [5]. Accordingly, it has been shown that all dendrimer families exhibit non-spherical and shape-persistent structures, with a molecular fractal dimension close to 2.5 and an invariant sur-

face fractal dimension approximately equal to 2, regardless the number of generations (branches) composing the molecular geometry.

In the present letter, we propose a new class of macromolecules that are also highly branched, but possess intrinsic disorder in their compositional and structural conformation. Here we use percolation as a model for disorder. Due to its simplicity, the percolation theory [6, 7] has been extensively applied to represent disordered materials in several research fields of scientific and technological relevance, such as condensed matter physics [8], flow through porous media [9], and heterogeneous chemistry [10, 11, 12, 13], among others. More precisely, percolation is a purely geometric model in the sense that we have to populate all lattice sites (or bonds) with a prescribed probability  $p$ . For small values of  $p$ , only finite clusters are present. By increasing  $p$ , one can find a threshold or a critical value  $p_c$  for which an “infinitely” connected object, the *spanning cluster*, is generated. In fact, the critical geometry of the spanning cluster [6, 11] is an example of random fractal that has been frequently used as a representation for real disordered systems. The aim here is to investigate through molecular mechanics simulations the geometrical properties of hydrocarbon molecules generated from carbon mantles subjected to site percolation disorder.

Starting from a square or an hexagonal lattice of size  $L$ , we extract the spanning cluster and assign to each site a carbon atom that is connected by single bonds to its nearest neighbors. The valence of each carbon in the cluster is then adjusted to 4 by adding the necessary hydrogen atoms, so that, in average, a hydrocarbon with fractional stoichiometry is produced, namely,  $\mathbf{C}_x\mathbf{H}_y$ . The bond length in the initial configuration of this molecule is set to an arbitrary guess value (e.g., 1Å) and a molecular mechanics method is applied to optimize the molecular

geometry [1]. Molecular mechanical force fields use the equations of classical mechanics to describe the potential energy surfaces and physical properties of molecules. Under this framework, a molecule is viewed as a collection of atoms that interact with each other by simple analytical functions. Here we apply the standard **MM+** force field [14] to obtain the optimized geometry for each realization of the percolating hydrocarbon. For comparison, a limited number of computational simulations have also been performed with a more realistic approach, namely, the **PM3** semi-empirical and self-consistent-field molecular orbital method [15]. For all practical purposes, the relative differences found between the geometrical properties calculated here resulting from the **PM3** technique and those obtained using the **MM+** molecular mechanics are always smaller than 3%.

In Fig. 1a we show the the original square lattice of carbon sites (planar) and the optimized geometries computed for a carbon mantle that is fully occupied ( $p = 1$ ). When submitted to the optimization procedure, the molecule bends spontaneously to assume the shape of a corrugated tile. In the case of an hexagonal lattice, the resulting molecular structure remains planar. The structures shown in Figs. 1b and 1c correspond to typical configurations of hydrocarbons mantles generated from square and hexagonal lattices, respectively, but now with the probability  $p$  set right above the critical percolation point  $p_c$ .

We performed simulations for square and hexagonal lattices generated at the critical point ( $p_c \approx 0.593$  and  $0.696$ , respectively), and with linear sizes ranging from  $L = 10$  to  $32$ . In the case of the square lattice, for each linear size  $L = 12, 15, 18, 21, 24, 27$ , and  $30$ , we used 300, 300, 150, 150, 80, 80, and 50 realizations, respectively. For the hexagonal geometry, the calculations have been carried out with 300, 150, 150, 80, 80, and 50 realizations for  $L = 10, 14, 18, 22, 26$ , and  $30$ , respectively. For each realization, once the convergence for the minimum energy structure is numerically attained, we compute a set of relevant geometrical properties that are then averaged over all samples of same size  $L$ . For instance, the radius of gyration  $R_g$  represents a meaningful measure to characterize objects of complicated geometry [6]. It is defined here as  $R_g^2 \equiv \sum_{i=1}^{N_a} |\mathbf{r}_i - \mathbf{r}_0|^2 / N_a$ , where  $N_a$  is the number of atoms,  $\mathbf{r}_0 \equiv \sum_{i=1}^{N_a} \mathbf{r}_i$ , and  $\mathbf{r}_i$  is the position of each atom  $i$  in the molecule, regardless of its type, i.e., hydrogen or carbon. The results shown in Fig. 2 clearly indicate that the radius of gyration displays a typical power-law behavior for both networks topologies,

$$R_g \sim M^{1/d_f}, \quad (1)$$

where  $M$  is the average molecular weight and  $d_f$  is the fractal dimension of the disordered molecules. The best fits to the data yield exponents that are statistically similar, namely,  $0.40 \pm 0.03$  and  $0.38 \pm 0.02$  corresponding to the fractal dimensions  $d_f = 2.50$  and  $2.63$ , for the square and hexagonal lattices, respectively. Considering the small sizes of the lattices employed in the simulations

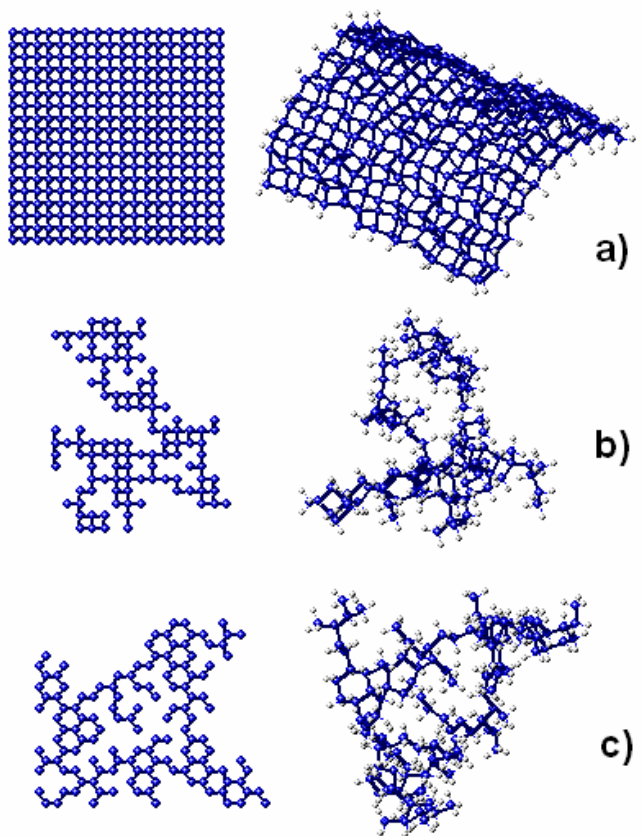


FIG. 1: (a) Hydrocarbon mantle of size  $L = 18$  generated from a fully occupied square lattice ( $p = 1$ ). The hydrocarbon chains on the left are the initial two-dimensional structures used in the optimization procedure, while those on the right are the corresponding three-dimensional topologies resulting from the molecular mechanics simulations. (b) The same as in (a), but for a value of  $p$  right above the critical percolation point  $p_c$ . (c) The same as in (b), but for an hexagonal lattice topology.

due to computational limitations, the agreement between these two exponents suggests that the complex geometry of percolating hydrocarbons may constitute a single class of universality.

At the microscopic scale it is important to determine the volume and surface of a molecule. Here we use the concept of van der Waals volume (surface) which is the sum of the volume (surface) of each atom composing a molecule, calculated as a sphere with the corresponding van der Waals radius. By definition, the van der Waals radii are simply the radii of the spheres connecting two non-bonded atoms [1]. The inset of Fig. 2 shows the log-log plot of the van der Waals volume  $V_W$  against the size  $L$  of the system for both square and hexagonal lattices. From the least-square fits to the two data sets we observe that the results for both lattice topologies can be well described by the scaling relation,  $V_W \sim L^{d_W}$ , where  $d_W$  is the critical exponent. If we consider that each carbon gives approximately the same contribution to the overall

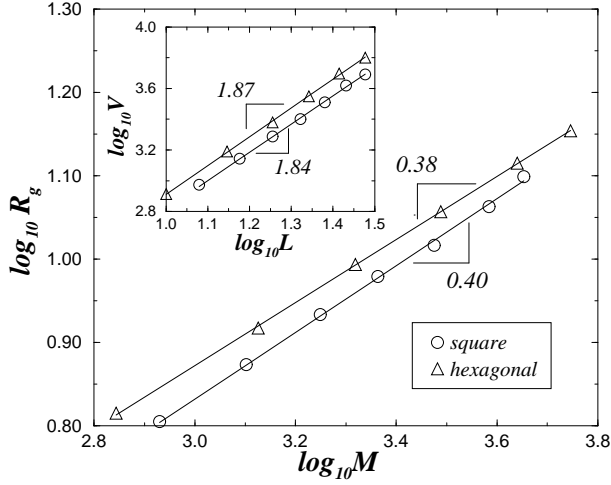


FIG. 2: Logarithmic plot showing the dependence of the radius of gyration  $R_g$  on the average molecular weight  $M$  of percolating hydrocarbons generated from square (circles) and hexagonal (triangles) lattices. The straight lines are the least-square fits to the data with the numbers indicating the slopes,  $0.40 \pm 0.03$  (circles) and  $0.38 \pm 0.02$  (triangles). The inset shows the log-log plot of the van der Waals volume against the linear dimension of the system for square (circles) and hexagonal (triangles) lattices.

volume of the molecule, the values  $d_W = 1.84 \pm 0.03$  and  $1.87 \pm 0.02$  obtained for the square and hexagonal lattice, respectively, can be readily compared with the fractal dimension of the spanning cluster at the critical percolation point, which is  $\approx 1.89$  in two dimensions [6]. The small discrepancies found here are due to finite-size effects as well as the presence of the hydrogens atoms necessary to balance the valence of the carbon sites.

As already mentioned, the investigation of molecular volume and surface is essential for the development of many chemical processes of scientific and technological relevance. Indeed, the molecular architecture can play a major role in determining the potential application and efficiency of functional macromolecules [5, 16]. In relation to that, the concepts of solvent accessible surface  $A_s$  and volume  $V_s$  [17] have been extensively used to characterize and compare the geometrical aspects of the interaction between a molecule and different types of solvent. As depicted in Fig. 3, the  $A_s$  is obtained by rolling a spherical probe of diameter  $2r_p$  corresponding to the size of the solvent (e.g., water or ethanol) on the van der Waals surface ( $A_W$ ) of the molecule. The  $V_s$  is the volume for which the boundary is the  $A_s$ . Since macromolecules like the percolating hydrocarbons studied here contain small gaps, pockets and clefts which are sometimes too small to be penetrated even by a solvent molecule like water, the  $A_s$  becomes gradually smoother as the size of the solvent used for probing increases. In the limiting case where  $r_p$  is set to zero, we recover the  $A_W$  of the molecule.

In Fig. 4 we show the log-log plot of the average accessible volume  $V_s$  against the linear size of percolating hydrocarbons gen-

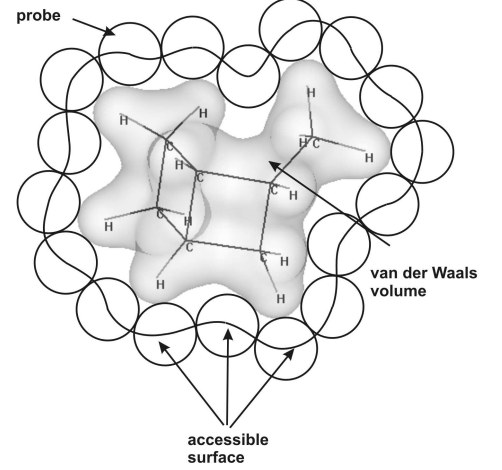


FIG. 3: The solvent accessible surface and volume of each realization of a percolating hydrocarbon are obtained by rolling a spherical probe of radius  $r_p$  on its van der Waals surface. For each lattice topology (square or hexagonal) and a given value of the linear dimension  $L$ , the average surface  $A_s$  and volume  $V_s$  are calculated from several realizations of the disordered molecules.

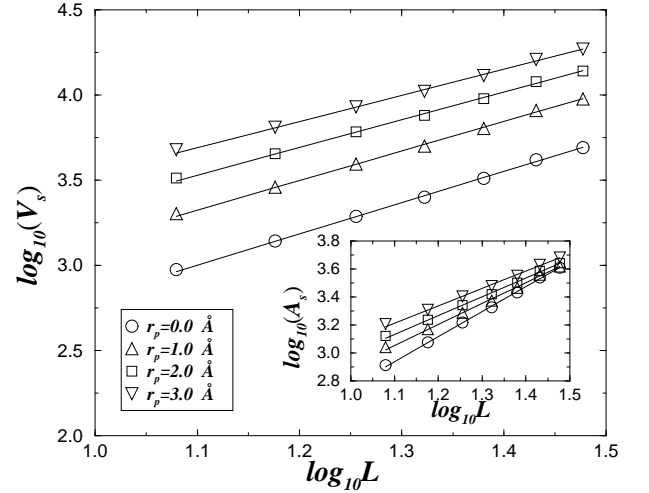


FIG. 4: Log-log plot of the variation of the average accessible volume  $V_s$  with the linear dimension  $L$  for four different values of the solvent probe radius  $r_p$ . The inset shows the same variation, but for the average accessible surface  $A_s$ . The straight lines are the best fits to the data sets of the scaling relations  $A_s \propto L^{\alpha_A}$  and  $V_s \propto L^{\alpha_V}$ , with the slopes corresponding to the exponents  $\alpha_A$  and  $\alpha_V$ . These results are for percolating hydrocarbons generated from a square lattice topology.

erated from square lattices, and calculated for four different values of  $r_p$ . These results provide clear evidence that the  $V_s$  of such disordered molecules increases as a power-law,

$$V_s \sim L^{\alpha_V}, \quad (2)$$

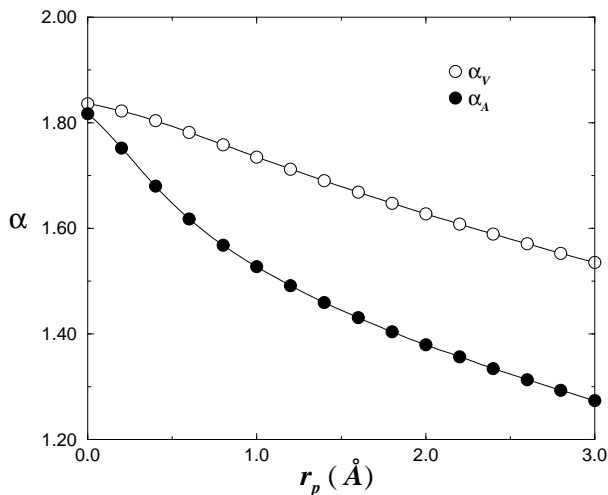


FIG. 5: Dependence of the scaling exponents  $\alpha_A$  and  $\alpha_V$  on the solvent probe radius  $r_p$  for percolating hydrocarbons extracted from a square lattice.

with an exponent  $\alpha_V$  that significantly depends on the size  $r_p$  of the probing molecule. The inset of Fig. 4 shows that the  $A_s$  also follows a power-law,  $A_s \sim L^{\alpha_A}$ , with an exponent  $\alpha_A$  that is, like in the  $V_s$  case, nonuniversal with respect to the solvent radius. We find an entirely similar behavior for both  $V_s$  and  $A_s$  obtained from molecular mechanics simulations performed with critical hexagonal lattices.

Figure 5 shows the dependence of  $\alpha_V$  and  $\alpha_A$  on the radius  $r_p$  for the case of the square topology. Starting from values that are close to the fractal dimension of the spanning cluster in two-dimensions, both exponents decrease monotonically with  $r_p$ , reflecting the gradual smoothness of the  $A_s$  as the size of the solvent molecule increases. In all cases, we find a maximum relative deviation of 5% between scaling exponents of square and hexagonal lat-

tices computed at the same value of  $r_p$ . As expected, these systems belong to the same universality class, despite the difference in the details of their microscopic geometry as well as the fact that a larger contribution of hydrogen atoms is needed to balance the critical hexagonal molecules, in comparison to their square counterparts of same size. These results indicate that any type of physical or chemical interaction between a percolating hydrocarbon and a given molecule can be dramatically dependent on the molecule size. For instance, even if uniformly functionalized, these highly structured hydrocarbons may display enormous discrepancies in reactivity if the reagents have slightly different sizes.

In conclusion we have studied the average geometrical features of molecules generated from hydrocarbon mantles subjected to percolation disorder. Our results show that these nanostructures are self-similar and display a rich variety of scaling behavior in their solvent accessible volume and surface properties. We expect these disordered molecules to be experimentally feasible. As an important step in this direction, ultrathin sheet-like carbon nanostructures, also called carbon nanosheets, have been recently synthesized under high controllability by a plasma enhanced process of chemical vapor deposition [16]. Among other characteristics, these molecules have a very high surface-to-volume ratio and sharp edges which are attractive for fuel cells and micro-electronic technologies. Under a different perspective, Andrade *et al.* [18] proposed a growth mechanism for branched polymers where self-organization leads the system spontaneously to a percolation-like critical state that is entirely similar to the disordered molecules investigated here. In this study, a conceivable experimental scheme is suggested for the implementation of the method that could lead to the generation of percolation hydrocarbons.

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